

# **Measurements of Specific Heat Capacity and Hemispherical Total Emissivity of Refractory Metals Using a Feedback- Controlled Pulse-Heating Technique <sup>1</sup>**

T. Matsumoto<sup>2,4</sup>, A. Ono<sup>2</sup>, and G. Barreiro<sup>3</sup>

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<sup>1</sup> Paper presented at the Fourteenth Symposium on Thermophysical Properties,  
June 25-30, 2000, Boulder, Colorado, U. S. A.

<sup>2</sup> National Research Laboratory of Metrology,  
1-1-4 Umezono, Tsukuba, Ibaraki 305-8563, Japan.

<sup>3</sup> Guest Scientist from National Center of Metrology,  
km 4,5 Carretera a Los Cues, Municipio el Merques C. P. 76900, Queretaro, Mexico

<sup>4</sup> To whom correspondence should be addressed.

## **ABSTRACT**

A new technique for measuring specific heat capacity and hemispherical total emissivity of electrically-conducting materials at high temperatures using a feedback-controlled pulse-heating technique has been developed at NRLM (National Research Laboratory of Metrology). This technique is based on a quick resistive heating of a strip sample up to a preset high temperature and then keeping the sample at that temperature for a short time (about 500 ms).

In this technique, A computer-controlled feedback system was employed to control the heating current. The sample temperature was determined using a high-speed radiation thermometer and a laser-ellipsometer. Specific heat capacity and hemispherical total emissivity of the sample were calculated from measured quantities using a heat balance equation based on the Stefan-Boltzmann law.

Using the present technique, the specific heat capacity and hemispherical total emissivity of the four refractory metals, i.e., niobium, molybdenum, tantalum, and tungsten, were measured in the temperature range from about 1500 K to a higher temperature close to the melting point of each metal. In this paper, preliminary results on the four refractory metals are presented.

**KEY WORDS:** hemispherical total emissivity; high temperature; pulse heating technique; refractory materials; specific heat capacity.

## **1. INTRODUCTION**

As a result of the cooperative work between NRLM (National Research Laboratory of Metrology) and NIST (National Institute of Standards and Technology in U. S.), a new pulse-heating technique using a feedback-control of the heating current was developed at NIST [1],[2]. After the preliminary development, an advanced type of this measurement technique has been developed at NRLM [3].

This technique is based on rapid resistive self-heating of a strip sample up to a preset high temperature in about 200 ms, and then maintaining the sample at that temperature under brief steady-state condition for about 500 ms before switching off the current. From the data on current, voltage drop across the sample, and true temperature of the sample, measured during the “plateau” maintained by the feedback control system (part B in Fig. 1), the hemispherical total emissivity of the sample is computed based on the Stefan-Boltzmann law. Then, the specific heat capacity is computed from the measured quantities in the heating phase from room temperature to the preset temperature.

Using this technique, the hemispherical total emissivity and specific heat capacity of the four refractory metals, i.e., niobium, molybdenum, tantalum, and tungsten were measured, and preliminary results on these materials are given.

## **2. PRINCIPLE OF THE MEASUREMENT**

The details of the measurement technique and apparatus are described in elsewhere [1],[3]. The heat balance equation for the effective sample between a pair of voltage probes is given by eq. (1).

$$C_p m \frac{dT_s}{dt} = EI - A_s \epsilon_{ht} \mathbf{s} (T_s^4 - T_e^4) \quad (1)$$

where  $A_s$  is the surface area of the effective sample,  $C_p$  is the specific heat capacity of the sample,  $E$  is the voltage drop across the voltage probes,  $I$  is the current passing through the sample,  $m$  is the mass of the effective sample,  $t$  is time,  $T_e$  and  $T_s$  are the temperatures of the environment and the sample surface, respectively,  $\epsilon_{ht}$  is the hemispherical total emissivity of the sample surface, and  $\mathbf{s}$  is the Stefan-Boltzmann constant.

Under brief steady-state condition at high temperatures, electrical power imparted to the effective sample (middle portion) is almost equal to the power loss from the sample by thermal radiation. The heat loss by axial conduction to the both ends of the sample is considered very small in comparison with that by radiation in such a rapid experiment. The contribution of the axial heat conduction to measurements were examined in the earlier work [1]. Based on above assumptions, eq. (1) written in the steady state yields the hemispherical total emissivity:

$$\epsilon_{ht} = EI / \{ A_s \mathbf{s} (T_s^4 - T_e^4) \} \quad (2)$$

Hemispherical total emissivity is computed using eq. (2) at each data point of experimental quantities ( $E$ ,  $I$ , and  $T_s$ ) on a plateau. A final value for the hemispherical total emissivity at the plateau temperature is then obtained by averaging the individual results over a finite time period. Usually, the averaging period (part C in Fig. 1) is less than the total plateau length (typically, 200 ms).

In a typical series of experiments, a pulse experiment with a temperature plateau was

repeated (10-20 times) on a sample with increasing the plateau temperature. The hemispherical total emissivities obtained at all plateau temperatures in a series of experiment were fitted by a linear or quadratic function of temperature.

Using this emissivity function, a specific heat capacity is computed for each data point in the heating phase (part A in Fig. 1) in each pulse experiment based on eq. (1). Then, a final fitted function for specific heat capacity is obtained by applying the least-squares-method for overall specific heat capacities computed in a series of experiments.

### **3. MEASUREMENT APPARATUS**

The high current to heat the sample was supplied from a condenser bank (63 V and 16 F) and regulated by a solid-state switch, which consists of parallel-connected FETs (field effect transistors). This switch rapidly adjusts the current level from zero to the maximum rating in response to an applied control voltage.

The feedback control during an experiment, as well as data acquisition, was performed using a personal computer with an A/D (analog-to-digital) and a D/A (digital-to-analog) converters of 16-bit voltage precision. Four voltages, i.e., (1) an output voltage of the radiation thermometer and three voltage differences across (2) the standard resistor, (3) the voltage probes, and (4) the current switch, were sampled by the A/D converter and recorded in the computer memory every 100  $\mu$ s. Simultaneously with the data acquisition and at the same sampling rate, an appropriate control voltage was computed by the PID (proportional, integral, and differential) control program on the computer and transferred to the current switch in order to maintain the constant temperature.

A high-speed optical radiation thermometer, operating at 655 nm (bandwidth 15 nm),

was used to measure the surface radiance temperature of the sample. The target of the radiation thermometer was a circular area of 0.5 mm in diameter. The response time (63% response) of the radiation thermometer was about 200  $\mu$ s. The measuring range of the radiation thermometer was approximately from 1200 to 1900 K. Four neutral density filters (0.337, 0.106, 0.042, and 0.012 in transmittance) were used to extend the range to temperatures above 1900 K.

The true temperature of the sample,  $T_{\text{true}}$ , was computed from the measured output voltage of the radiation thermometer using the following equation based on the Planck's law.

$$T_{\text{true}} = c_2 / \{ A \text{Log} (\epsilon_{n\lambda} C / V_r) \} - B / A \quad (3)$$

where  $A$ ,  $B$ , and  $C$  are the characteristic constants of the radiation thermometer,  $c_2$  is the second radiation constant,  $V_r$  is the output voltage of the radiation thermometer, and  $\epsilon_{n\lambda}$  is the normal spectral emissivity of the sample.

The radiation thermometer was calibrated by measuring the spectral response of the output voltage in the range of wavelength from 350 to 1250 nm, and by measuring the output voltage against a fix-point black body of copper (1357.8 K).

In order to decide the true temperature of the sample, normal spectral emissivity of the sample was measured simultaneously with the other experimental quantities in every 0.5 ms using a high-speed laser-ellipsometer [4]. The measuring wavelength of the ellipsometer was 675 nm, which was the wavelength of a laser diode used for the ellipsometer.

Because the measuring wavelengths of the ellipsometer and the radiation thermometer were different, the measured values of spectral emissivity were corrected to correspond to

the wavelength of radiation thermometer. This procedure was performed by eq. (4) using the normal spectral emissivities of niobium [5], molybdenum [6], tantalum [7], and tungsten [8] given in the literature at several wavelengths and at the melting point.

$$\mathbf{e}_{I,\text{th}} = \mathbf{e}_{I,\text{el}} - (\partial \mathbf{e}_I / \partial I)_{\text{mp}} (I_{\text{el}} - I_{\text{th}}) \quad (4)$$

where  $\mathbf{e}_{I,\text{th}}$  is the corrected normal spectral emissivity at the measuring wavelength of the radiation thermometer,  $\mathbf{e}_{I,\text{el}}$  is the normal spectral emissivity measured by the ellipsometer,  $(\partial \mathbf{e}_I / \partial I)_{\text{mp}}$  is the wavelength-derivative of normal spectral emissivity at the melting point calculated from the results given in the literature, and  $I_{\text{el}}$  and  $I_{\text{th}}$  are the measuring wavelength of the ellipsometer and the radiation thermometer, respectively. The actual correction factors for niobium, molybdenum, tantalum, and tungsten between  $I_{\text{el}}$  and  $I_{\text{th}}$  were 0.97 %, 0.93 %, 0.89 %, and 0.90%, respectively.

#### 4. MEASUREMENTS AND RESULTS

Measurements were conducted on several strip-shaped samples of niobium, molybdenum, tantalum, and tungsten. The specifications of the measured samples are listed in Table I. The surfaces of the most of the samples were polished at a surface roughness (Rmax) less than 100 nm. The distance between a pair of voltage probes attached separately on the sample surface was fixed constant at about 40 mm, that is, the ends of the probes slid on the surface even the sample moved due to thermal expansion. The surface area,  $A_s$ , in eq. (1) calculated based on the sample dimensions at room temperature regardless thermal expansion. However, measured quantities were not corrected of thermal expansion.

All experiments were conducted in vacuum at about  $5 \times 10^{-4}$  Pa. In a typical series of

experiments, an experiment with a pulse heating using the feedback control was repeated on a sample with increasing the plateau temperature by about 100 K over the range approximately from 1500 K to a maximum temperature point lower than the melting point by about 100-200 K. In order to clean the sample surface, each sample was preheated in vacuum up to 1700-2000 K several times before a series of experiments.

Variations of the true temperature and heating current during a typical experiment are shown in Fig. 2. In this experiment, a tantalum sample was heated from room temperature to 2260 K in 100 ms, and maintained at that temperature for approximately 400 ms. It can be seen that the current required to maintain the temperature constant is much smaller than the current required during the rapid heating. The sample was maintained at the constant temperature within  $\pm 0.1$  K, which was almost the same level with the random signal noise on temperature.

Fig. 3 shows an example of normal spectral emissivity of tungsten measured with the laser-ellipsometer. Each data point represents an averaged value in a plateau. The most results on normal spectral emissivity of the four metals showed gradual decrease with temperature. These results were used to compute the true temperature based on eq. (3).

The results on hemispherical total emissivity of niobium, molybdenum, tantalum, and tungsten are shown in Fig. 4, Fig. 5, Fig. 6, and Fig. 7, respectively. Each data point represents an averaged emissivity value calculated using eq. (2) in a plateau. The solid curves represent quadratic functions fitted to each sample using the least-mean-squares method. These emissivity functions were used to calculate specific heat capacity using eq. (1). In these figures, earlier results on hemispherical total emissivity using the feedback-

control technique [1],[2] are also shown in broken curves.

The results on specific heat capacity of the same samples calculated using eq. (1) are shown in Fig. 8, Fig. 9, Fig. 10, and Fig. 11, respectively. Each curve represents the final cubic functions fitted to the results obtained in about 10 series experiments on a sample. Although they are not shown, the deviation of the result of each experiment on a sample from the final function on the figures was almost within  $\pm 1$  % for all samples of the four metals. In these figures, the earlier results on niobium [9], molybdenum [10], tantalum [11] and tungsten [12] given in the literature are shown by the broken curves.

## 5. DISCUSSIONS AND CONCLUSIONS

Present results on hemispherical total emissivity show higher values than the earlier results by about 8 % for niobium, 5 % for molybdenum, 8 % for tantalum, and 10 % for tungsten. Differences in emissivity between different samples of the same material were almost in the range of 10 % for the four metals.

In general, it is well understood that the optical properties of metallic surfaces are very sensitive to surface condition, such as, surface roughness, contamination, and oxidation. Hence, emissivities of metals given in literature sometimes show large scatter over 20 % (for an example, [2]). Some extent of the scatter in the present results therefore may be attributed to the difference in surface condition.

However, what should be noticed is that all present results on hemispherical total emissivity show positive systematic deviations from the earlier results although the most of the sample surfaces were polished well. In addition, significant difference due to surface roughness was not observed between the two different groups of samples, that is, Ta-1 and

2 (as received), and Ta-3 (polished). These results contradicts the generally-accepted idea that a smoother surface yields a smaller emissivity if the surface is clean enough. We consider that there might be unknown reasons for the unreasonable behaviors in emissivity.

For the results on specific heat capacity of the four metals, the difference between different samples of the same material were almost within a range of 5 %. The averaged deviations of the present results from those reported in the literature were about +8 % for niobium, +1 % for molybdenum, +2.5 % for tantalum, and +2 % for tungsten. Considering that the maximum inaccuracy reported in the literature was 3% for the four metals, the agreements between the present results and those in the literature are reasonably good except for niobium. However, as is seen in the results on hemispherical total emissivity, the most of the results on specific heat capacity also show positive deviation from those in the literature.

Because of these unreasonable disagreements, we consider the present results are still “preliminary”, and should not be regarded as a reference. In order to produce more reliable results, further systematic surveys on overall inaccuracy due to measurement technique itself and stability of sample condition at high temperature are required.

## **ACKNOWLEDGMENTS**

Late Dr. A. Cezairliyan of NIST gave us valuable advises in the development of the present measurement technique. The radiation thermometer was calibrated by Dr. F. Sakuma of NRLM. The authors greatly appreciate their supports to the present work.

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Table I. Specifications of the Measured Samples

Material - Sample No.	Thickness × Width × Length (mm <sup>3</sup> )	Surface Roughness (Rmax)	Puerility
Nb - 1, 2, 3	$0.3 \times 5 \times 66$	$< 100 \mu\text{m}$	99.9 %
Mo - 1, 2, 3	$0.3 \times 5 \times 80$	$< 100 \mu\text{m}$	99.95 %
Ta - 1, 2	$0.3 \times 5 \times 80$	as received	99.95 %
Ta - 3	$0.3 \times 5 \times 80$	$< 100 \mu\text{m}$	99.95 %
W - 1, 2, 3	$0.3 \times 5 \times 80$	$< 100 \mu\text{m}$	99.95 %

## FIGURE CAPTIONS

- Fig. 1 Temperature-time diagram in an experiment using the feedback control technique.
- Fig. 2 Variations of temperature and current in a typical experiment on a tantalum sample.
- Fig. 3 Normal spectral emissivity of tungsten measured with the laser-ellipsometer.
- Fig. 4 Hemispherical total emissivity of niobium obtained in the present measurements.
- Fig. 5 Hemispherical total emissivity of molybdenum obtained in the present measurements.
- Fig. 6 Hemispherical total emissivity of tantalum obtained in the present measurements.
- Fig. 7 Hemispherical total emissivity of tungsten obtained in the present measurements.
- Fig. 8 Specific heat capacity of niobium obtained in the present measurements.
- Fig. 9 Specific heat capacity of molybdenum obtained in the present measurements.
- Fig. 10 Specific heat capacity of tantalum obtained in the present measurements.
- Fig. 11 Specific heat capacity of tungsten obtained in the present measurements.

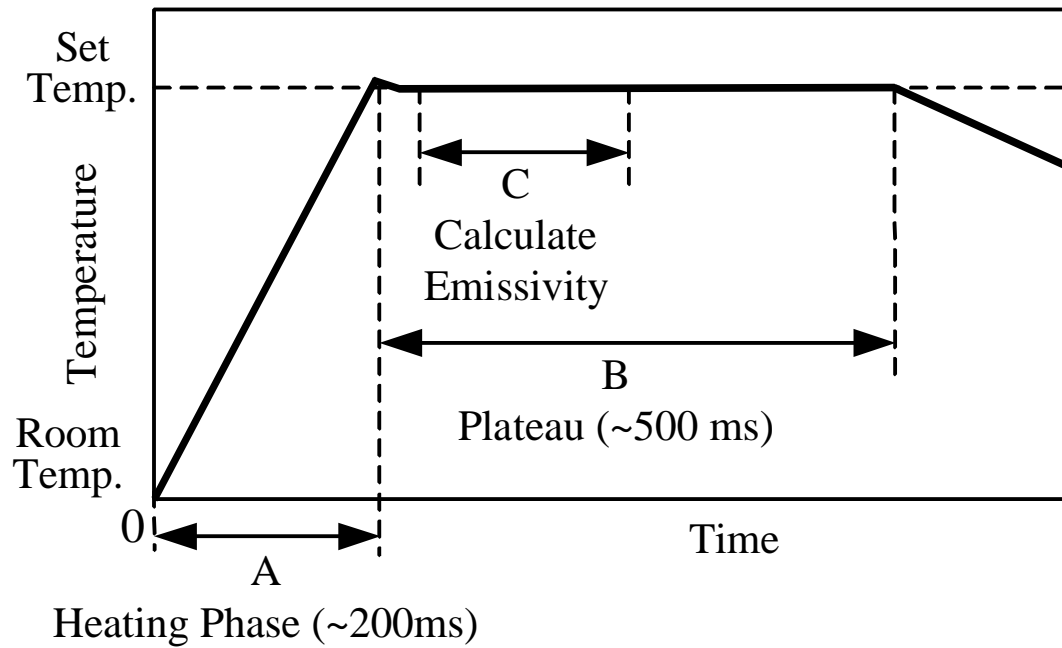


Fig. 1 Temperature-time diagram in an experiment using the feedback control technique.

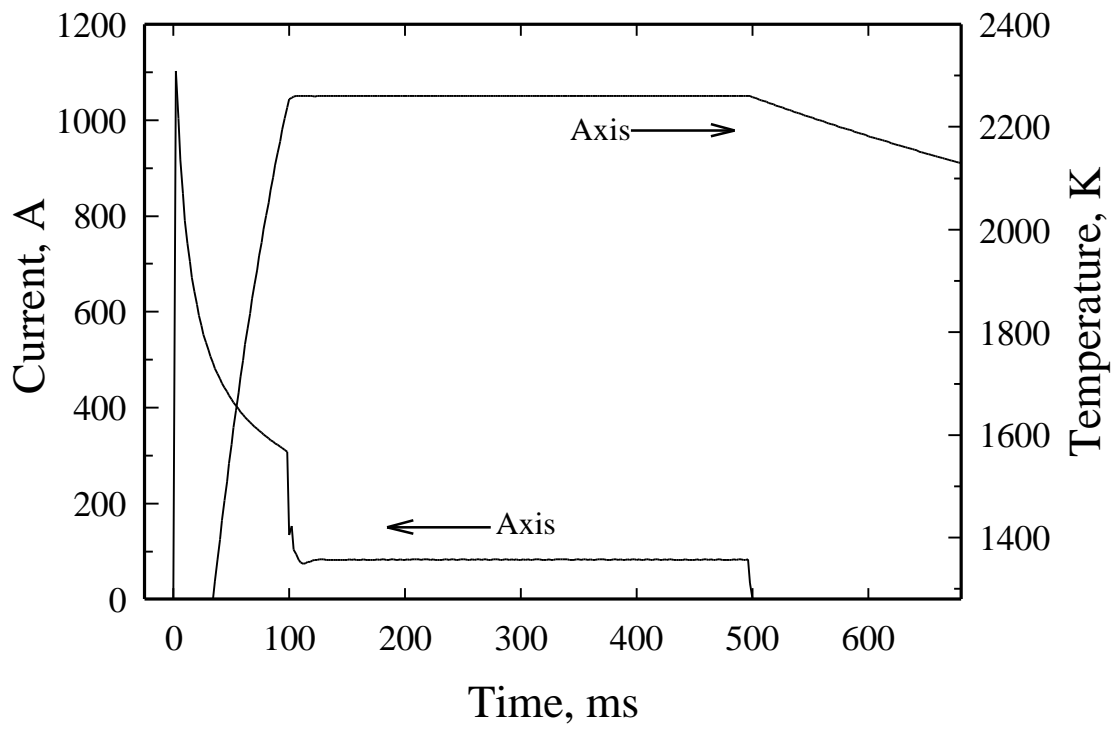


Fig. 2 Variations of temperature and current in a typical experiment on a tantalum sample.

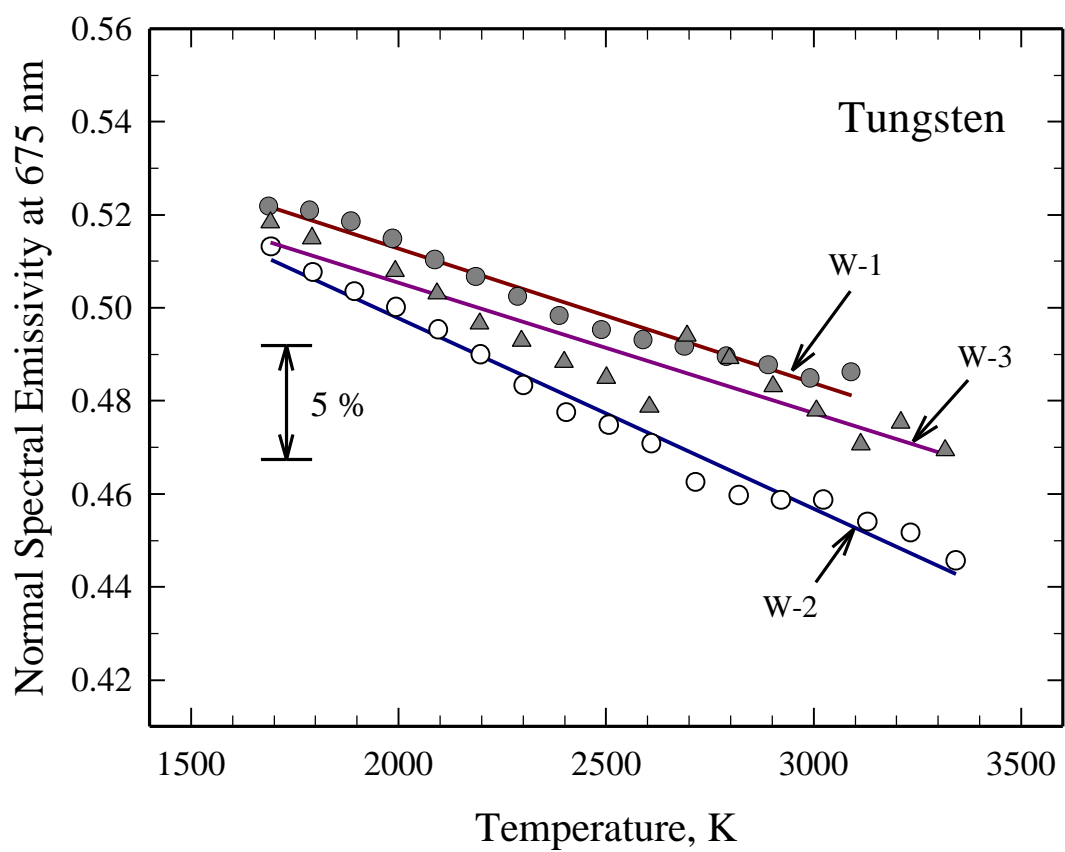


Fig. 3 Normal spectral emissivity of tungsten measured with the laser-ellipsometer.

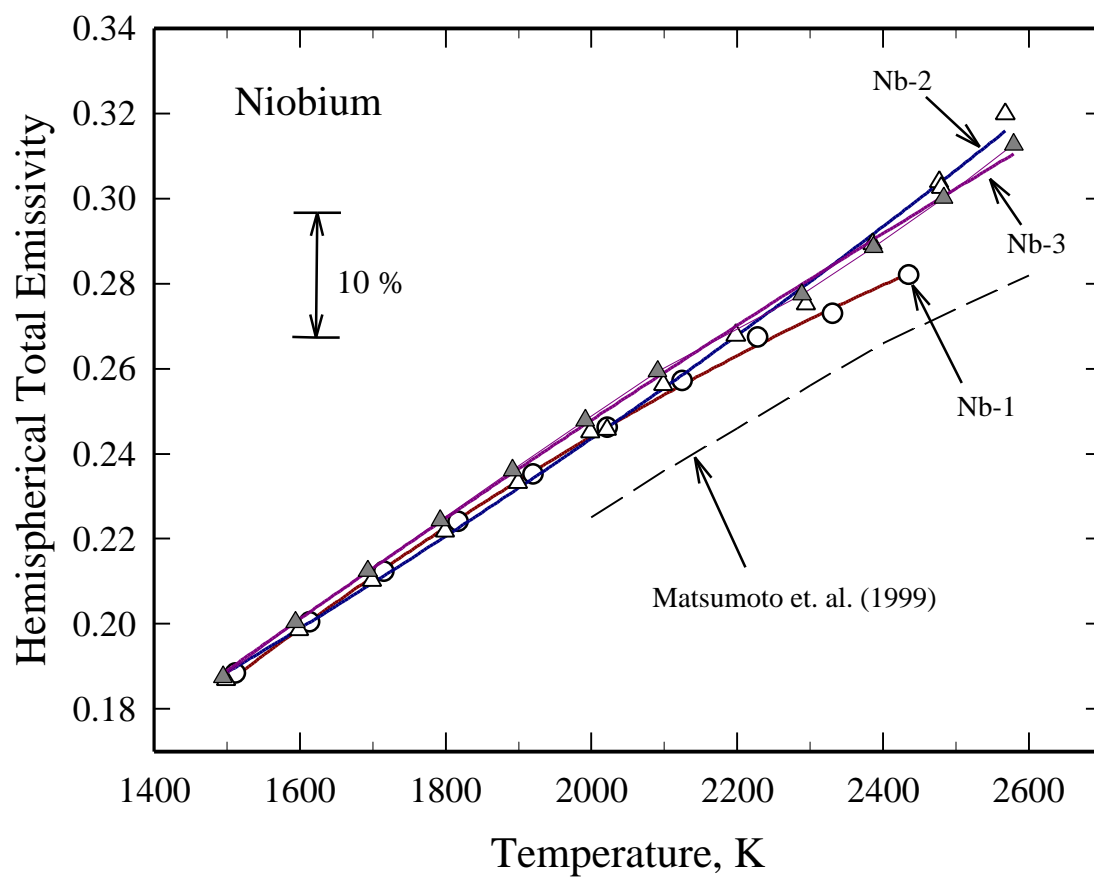


Fig. 4 Hemispherical total emissivity of niobium obtained in the present measurements.

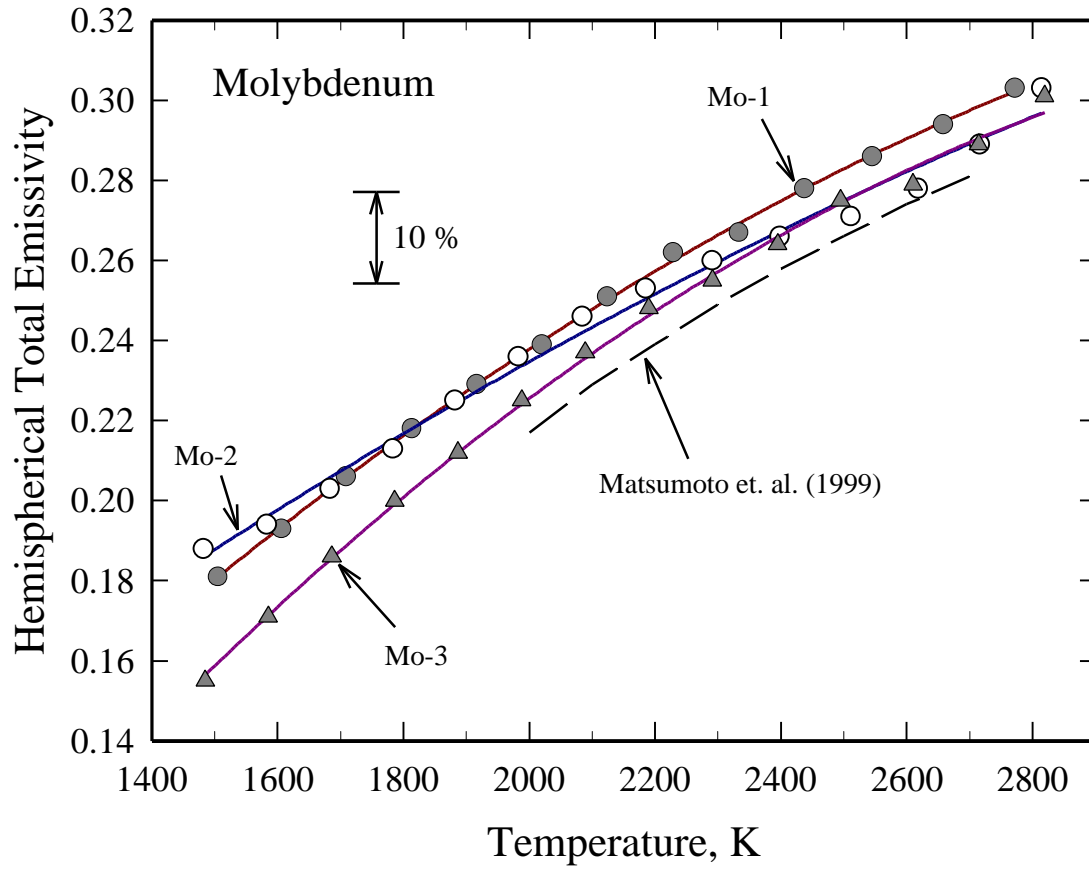


Fig. 5 Hemispherical total emissivity of molybdenum obtained in the present measurements.

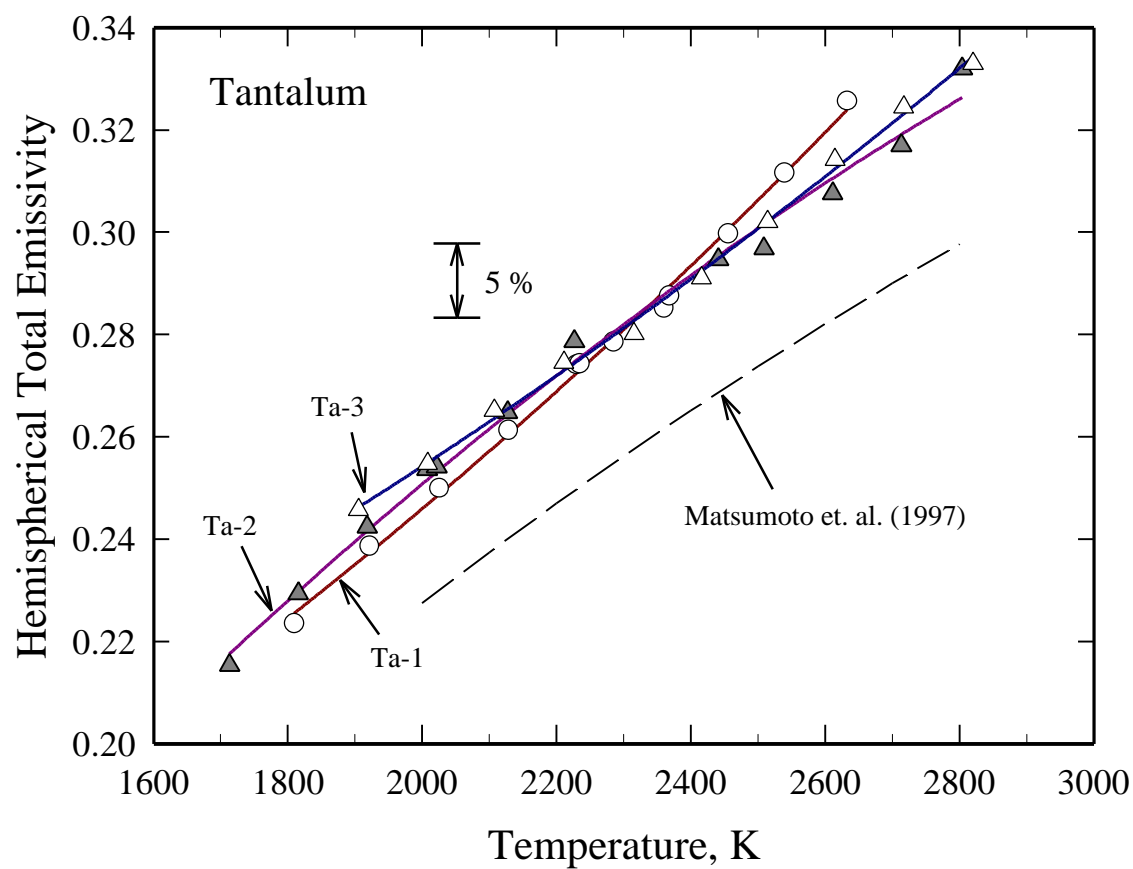


Fig. 6 Hemispherical total emissivity of tantalum obtained in the present measurements.

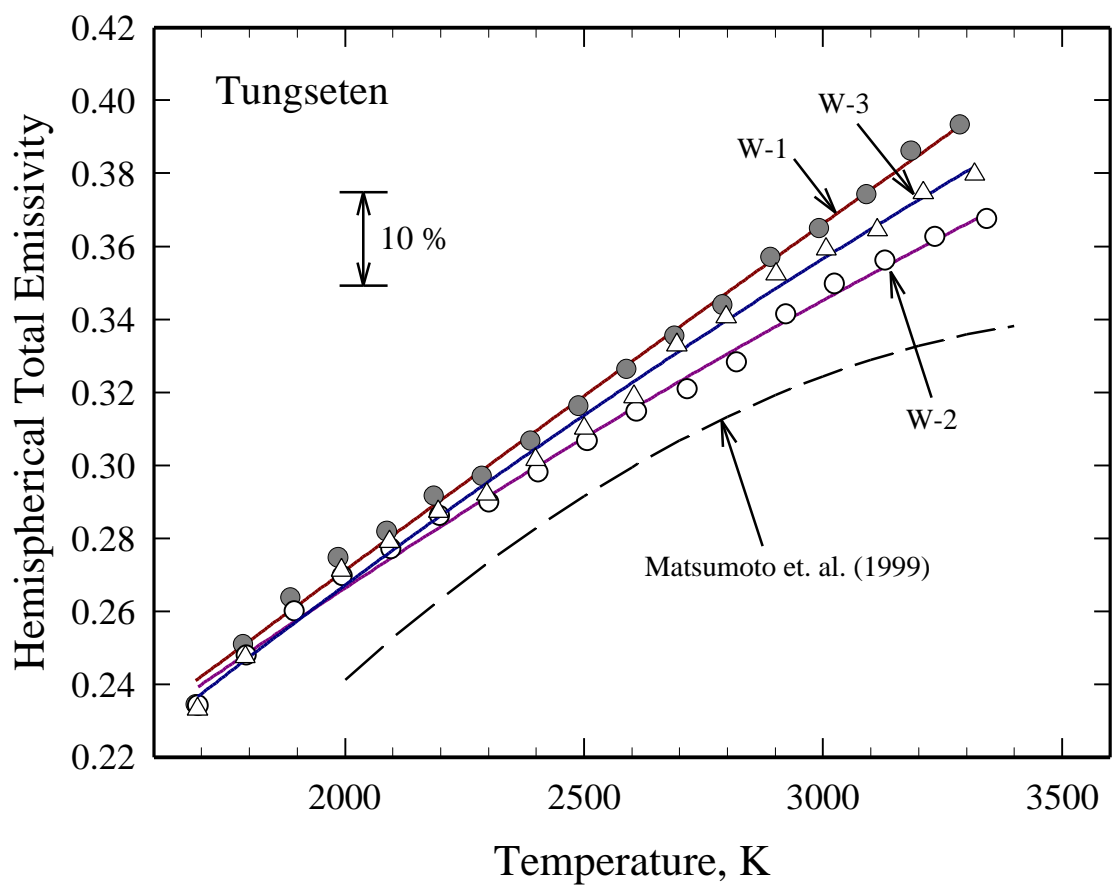


Fig. 7 Hemispherical total emissivity of tungsten obtained in the present measurements.

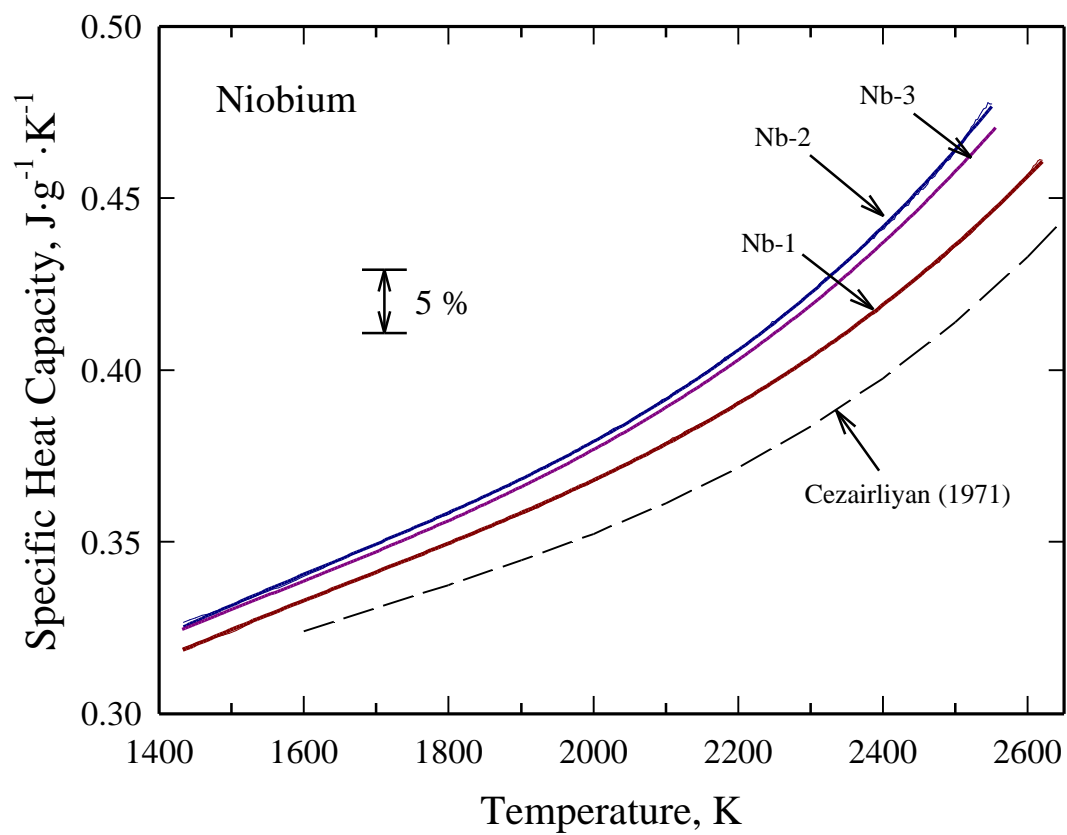


Fig. 8 Specific heat capacity of niobium obtained in the present measurements.

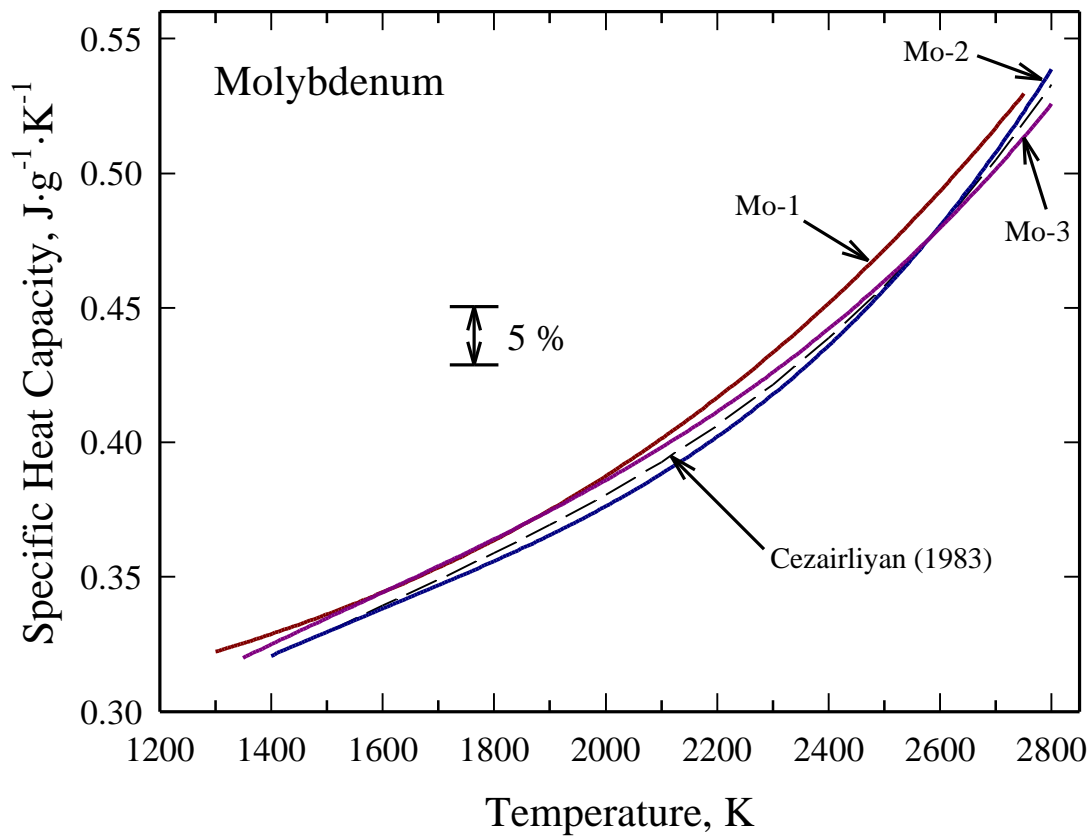


Fig. 9 Specific heat capacity of molybdenum obtained in the present measurements.

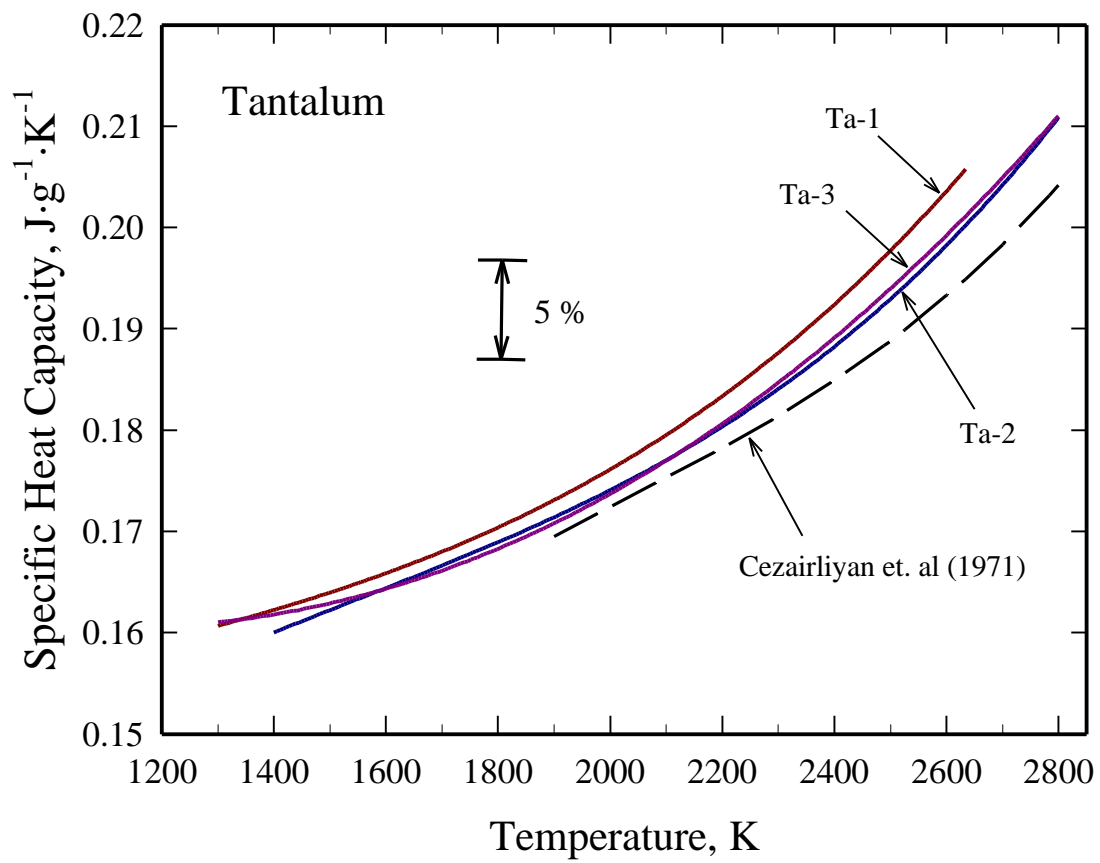


Fig. 10 Specific heat capacity of tantalum obtained in the present measurements.

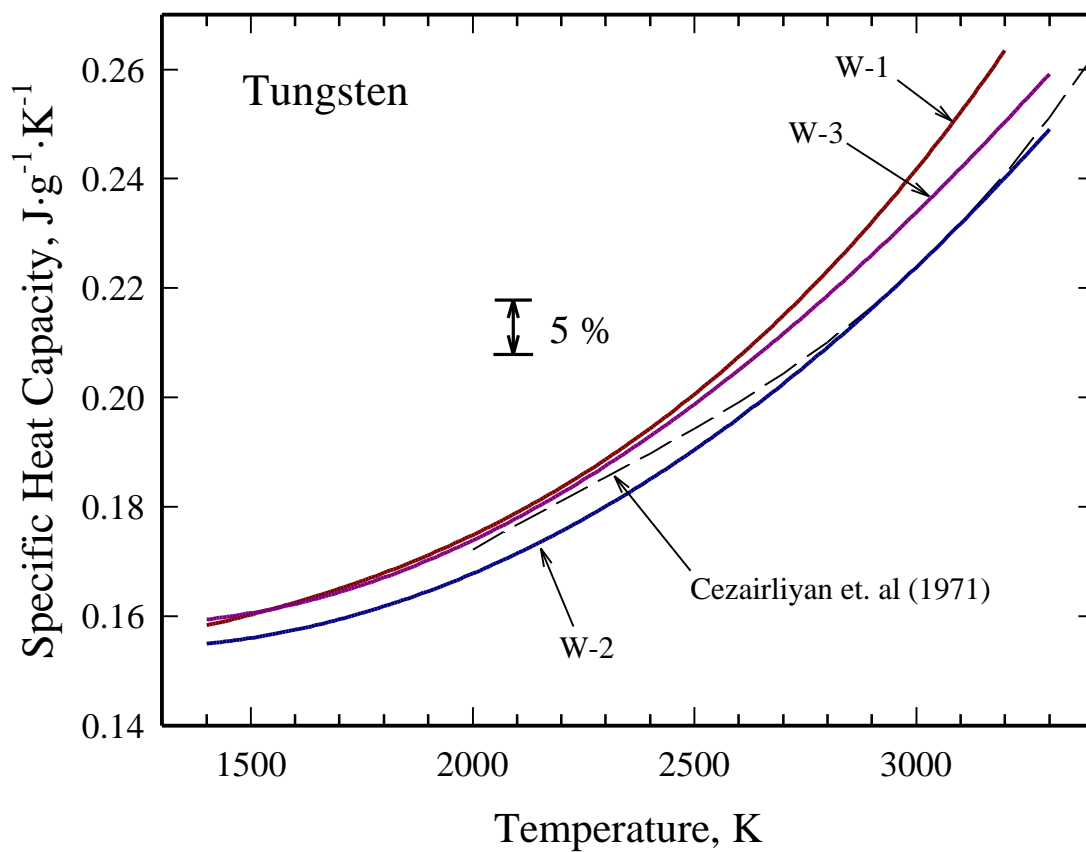


Fig. 11 Specific heat capacity of tungsten obtained in the present measurements.